

Emission factors of PAHs, methoxyphenols, levoglucosan, elemental carbon and organic carbon from simulated wheat and Kentucky bluegrass stubble burns

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Abstract

Emission factors (EFs) of pollutants from post-harvest agricultural burning are required for predicting downwind impacts of smoke and inventorying emissions. EFs of polycyclic aromatic hydrocarbons (PAH), methoxyphenols (MP), levoglucosan (LG), elemental carbon (EC) and organic carbon (OC) from wheat and Kentucky bluegrass (KBG) stubble burning were quantified in a US EPA test burn facility. The PAH and MP EFs for combined solid + gas phases are $17 \pm 8.2 \text{ mg kg}^{-1}$ and $79 \pm 36 \text{ mg kg}^{-1}$, respectively, for wheat and $21 \pm 15 \text{ mg kg}^{-1}$ and $35 \pm 24 \text{ mg kg}^{-1}$, respectively, for KBG. LG, particulate EC and artifact-corrected OC EFs are $150 \pm 130 \text{ mg kg}^{-1}$, $0.35 \pm 0.16 \text{ g kg}^{-1}$ and $1.9 \pm 1.1 \text{ g kg}^{-1}$, respectively, for wheat and $350 \pm 510 \text{ mg kg}^{-1}$, $0.63 \pm 0.056 \text{ g kg}^{-1}$ and $6.9 \pm 0.85 \text{ g kg}^{-1}$, respectively, for KBG. Positive artifacts associated with OC sampling were evaluated and remedied with a two-filter system. EC and OC accounted for almost two-thirds of $\text{PM}_{2.5}$ mass, while LG accounted for just under 3% of the $\text{PM}_{2.5}$ mass. Since EFs of these pollutants generally decreased with increasing combustion efficiency (CE), identifying and implementing methods of increasing the CEs of burns would help reduce their emissions from agricultural field burning. PAH, OC and EC EFs are comparable to other similar studies reported in literature. MP EFs appear dependent on the stubble type and are lower than the EFs for hard and softwoods reported in literature, possibly due to the lower lignin content in wheat and KBG.

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1. Introduction

Combustion is one of the methods used to reduce post-harvest residues from wheat and Kentucky bluegrass (KBG) fields in eastern Washington (WA) and northern Idaho (ID). Over 45,000 ha of wheat

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and 20,000 ha of KBG were burned in these areas in 2002 (WA DOE, 2004; ISDA, 2003). Emission factors (EFs: the pollutant mass emitted per unit mass of dry stubble consumed by fire) are required for modeling the dispersion of smoke from these fires and for inventorying pollutant emissions.

Pollutants in smoke from agricultural burning include, among others, fine particulate matter ($PM_{2.5}$) and semi volatile organic compounds (SVOCs, present in solid and gas phases). $PM_{2.5}$ is known to affect respiratory health (Roberts and Corkill, 1998; Mar et al., 2004). Several polycyclic aromatic hydrocarbons (PAHs; classified as SVOCs) emitted during incomplete combustion are carcinogenic and are associated with mutagenicity (Seinfeld and Pandis, 1997; Roberts and Corkill, 1998; Ramdahl and Becher, 1982). EFs of these pollutants are required for modeling human exposure to them, with the intention of safeguarding public health.

Several methoxylated phenols (MPs; also classified as SVOCs), particularly syringyl and guaiacyl species, are used as markers of lignin combustion (Hawthorne et al., 1988; Simpson et al., 2005; Simoneit, 2002). 1,6-anhydro- β -D-glucopyranose, commonly known as levoglucosan (LG), is often reported along with MP measurements, as it is considered a marker of cellulose pyrolysis, and is mostly present in the solid phase (Hays et al., 2002, 2005; Schauer et al., 2001). MP and LG EFs are needed for developing source profiles for receptor models, which in turn can be used for assessing the contribution of biomass burning to air pollution episodes (Simoneit, 2002).

Elemental carbon (EC) and organic carbon (OC) can account for over 50% of the $PM_{2.5}$ mass in areas impacted by smoke from biomass burning (Reid et al., 2005; Seinfeld and Pandis, 1997). EFs of these aerosol components are required for compiling emissions inventories, for regulatory purposes.

Recently we reported $PM_{2.5}$ EFs from wheat and KBG burning (Dhammapala et al., 2006). While PAH, MP and LG emissions from burning wood and forest debris are documented, a recent review paper (Lemieux et al., 2004) shows few studies reporting emissions of PAHs from agricultural burning. Additionally, two studies involving wheat and KBG burns [Air Sciences Inc. (A.S.I.), 2003 and 2004, respectively] in eastern WA and northern ID provide limited PAH data. We are only aware of one study (Hays et al., 2005) detailing the MP and

LG emissions from agricultural burning, and part of the data in that study was collected during the experiments described in this paper.

Data on EC and OC emissions from agricultural burning are also scarce (Turn et al., 1997; Hays et al., 2005). It is known that a positive sampling artifact may substantially bias OC measurements (Kirchstetter et al., 2001; Subramanian et al., 2004; Turpin et al., 1991). However literature reporting OC EFs from biomass burns (e.g. Turn et al., 1997; Christian et al., 2003) does not mention an artifact correction, and as a result, the accuracy of the OC EFs is unknown.

The purpose of this work is to address these data needs by determining EFs of 19 PAHs (including all species on the former “priority PAH” list), 19 MPs (9 guaiacyl and 10 syringyl species, often reported in recent literature), LG, EC and OC from wheat and KBG stubble burning.

2. Methodology

Irrigated winter wheat (*Triticum aestivum* L., variety Madsen) and non-irrigated KBG (*Poa pratensis* L.) stubble was collected from fields in eastern WA and northern ID, respectively, between 5 and 15 days prior to burn experiments. The stubble moisture content in the field was approximately 9% on a wet basis, and ranged from 10% to 11% at the time of burning. Burn experiments were conducted during May and August 2001 (Campaigns 1 and 2, respectively), August 2003 (Campaign 3) and July 2004 (Campaign 4), in an enclosed, well-mixed, flow-through test burn chamber located at the US EPA in Research Triangle Park, NC (Dhammapala et al., 2006). Airflow into and circulation within the chamber were maintained to mimic open burn conditions (high O_2 and unimpeded ventilation) and minimize wall losses. During each burn, approximately 750 g of stubble, arranged to mimic post-harvest field orientation, was ignited manually with a propane torch and the chamber door closed immediately. Pollutant concentrations, chamber air flow rates, chamber temperatures and stubble mass loss rates were measured for calculation of EFs.

2.1. Sampling

For each burn experiment, emissions were sampled for approximately 20 min, until stubble mass loss and smoldering combustion ceased. The

sampling of CO₂, CO, hydrocarbons and integrated PM_{2.5} [the chamber concentrations of which ranged from 0.15–0.71% (v/v), 19–490 ppm, 2.2–60 ppm, and 0.40–51 mg m⁻³, respectively] are described in detail (Dhammapala et al., 2006). Particle phase SVOCs and LG were sampled with a low volume (LV: 5 L min⁻¹; Airmetrics Inc., Eugene, OR) PM_{2.5} sampler with 47 mm diameter Teflon filters (Whatman Inc., 40 µm thick, 2 µm pore size).

Polyurethane foam (PUF) plugs (URG Corp., Chapel Hill, NC), with a diameter of 1.5 cm and thickness of 3–4 cm, were placed in a silanized glass tube (Simpson et al., 2005) downstream of the Teflon filters to trap gas phase SVOCs. Prior to use, PUFs were cleaned twice in a Soxhlet extractor for 24 h in a 1:1 mixture of acetonitrile and ethyl acetate. Additional LV samplers with pre-heated (800 °C for 12 h) 47 mm diameter quartz filters (Whatman Inc., thickness 0.45 mm) were used for collecting PM_{2.5} samples for subsequent EC and OC determination.

The configurations of filters and PUFs in the LV samplers are shown in Fig. 1. See Table 1 for an inventory of samples collected. During Campaign 1, a dilution sampler was also operated to assess the chemical composition of PM_{2.5} (see Hays et al., 2005).

2.1.1. OC adsorption artifact

The adsorption of SVOCs on quartz filters gives rise to a positive OC sampling artifact, and this is corrected by subtracting the SVOC collected on the QbT filter, from the OC on the Q filter (Mader et al., 2003; Pang et al., 2002; Turpin et al., 1994; Eatough

et al., 1993). The negative artifact caused by SVOC volatilization off filters during sampling is assumed to be negligible (Pang et al., 2002; Mader et al., 2003). Since PAHs and MPs could be contained in the artifactual OC (Hays et al., 2005), quartz filters were not analyzed for solid phase SVOCs.

2.2. Analytical methods

The samples from Campaigns 1, 2 and 3 were analyzed for 16 PAHs at Eastern Washington University (EWU) in Cheney, WA, by gas chromatography–mass spectrometry (GC–MS). Samples from Campaign 4 were analyzed for 20 PAHs, 19 MPs and LG at the University of Washington (UW) in Seattle, WA, also by GC–MS. Since the GC–MS at UW and EWU were operated in selective ion and full scan modes, respectively, the analytical method at UW had a lower detection limit.

All glassware was silanized prior to use during SVOC analysis, to minimize MP and LG losses to glass surfaces (Simpson et al., 2004, 2005). The procedures for extraction, sample preparation and analysis of PAHs, LG and MPs have been described previously (Simpson et al., 2004, 2005; Dills et al., 2006). Briefly, samples were spiked with a known mass of deuterated standards and extracted by sonicating in 30 mL ethyl acetate containing 0.5% (v/v) triethylamine (TEA). Extracts were concentrated to 0.5 mL by evaporation under nitrogen in a turbvap concentrator (Zymark Corp., Hopkinton, MA), and internal standards (2,3-dimethoxyphenol, 4-chloro-2-methoxyphenol, bromosyringaldehyde

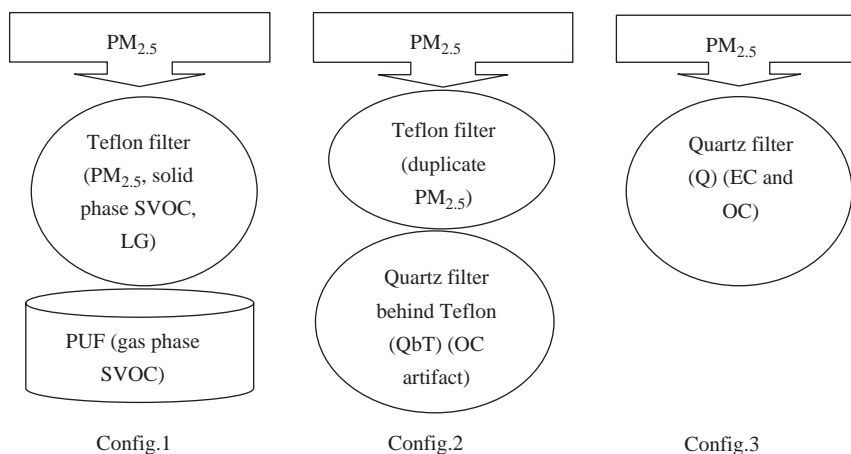


Fig. 1. Configuration of filters and PUFs in LV samplers. Each substrate was analyzed for the species indicated. See Section 2.1.1 for discussion on OC artifact.

Table 1

Number of samples collected using LV samplers. The numbers in square brackets are the number of burn experiments conducted. Numbers in parentheses are the # of Teflon filters combined prior to analysis at EWU, to obtain a detectable PAH mass

	Wheat stubble			KBG stubble	
	Campaign 1 [30]	Campaign 2 [31]	Campaign 4 [6]	Campaign 3 [30]	Campaign 4 [6]
Teflon _{Config.1}	30 (5)	31 (6) ^a	6 ^b	85 ^c	6 ^b
PUF _{Config.1}	–	–	4	8 ^c	6
Teflon _{Config.2}	1 ^d	– ^d	6	33	6
QbT _{Config.2}	1 ^d	– ^d	5	29	5
Q _{Config.3}	6 ^d	– ^d	5	33	5

^aTeflon filters from the last seven burns were combined.

^bOnly Campaign 4 samples were analyzed for LG.

^cAll SVOC data from the KBG burns of Campaign 3 were lost.

^dSome samplers malfunctioned and therefore limited the number of samples collected.

and trimethoxybenzene for MP analysis; benzene, 1,3,5-tris(1-methylethyl) for PAHs and 1,5-anhydro-D-mannitol for LG) were added. For LG and MP analyses, a portion of the extract was then derivatized with 10% (v/v) *N*-trimethylsilylimidazole, and a 4:3 solution of acetic anhydride and TEA, respectively. Samples were then injected into the GC–MS.

For EC and OC quantification, rectangular 1.5 cm² punches of the quartz filters were analyzed with a thermal optical transmittance (TOT) carbon analyzer (Sunset Labs Inc., Tigard, OR). The temperature program used is described in Pang et al. (2002).

2.3. Data validity and QA/QC measures

Secondary OC can be formed during downwind transport (Turpin et al., 1991). Reactions between solid phase PAH and O₃, and gas phase PAH and OH radicals can both result in PAH lifetimes of less than an hour (rate constants from Pöschl et al., 2001; Alebić-Juretić et al., 1990; Calvert et al., 2002). MPs have been reported to react with PAHs (Kjällstrand and Petersson, 2001; McDow et al., 1994). Therefore EFs of SVOCs presented here are valid at the point of emission only, and help assess the reactive organic species contributed to the atmosphere by biomass burning. Under this framework, dispersion and receptor models will need to account for variability in EFs and subsequent secondary reactions, for both SVOC and non-volatile OC.

Ozone has been reported to degrade filter-collected PAHs (Pöschl et al., 2001; Alebić-Juretić

et al., 1990). However, O₃ levels measured during the burn experiments conducted here were below the instrumental detection limit of 1 ppb, and are not expected to significantly influence PAH data.

Laboratory blanks were analyzed with every batch of field samples. Analyte concentrations in these blanks were either below detection limits, or were lower than the corresponding analyte concentrations in background samples from the chamber experiments. Based on background corrected concentrations of all individual species, the precision of field duplicates averaged 22% for both PAHs (eight sample pairs) and MPs (four sample pairs). For LG, the precision was 11%, based on one sample pair. The relative standard deviation (RSD) of triplicate laboratory analyses was 14% ($n = 12$), 12% ($n = 6$) and 6% ($n = 1$) for PAHs, MPs and LG, respectively.

The TOT method for EC and OC analysis assumes that the sample is evenly distributed across the quartz filter. TOT analyses on duplicate punches obtained from the same filter showed a high degree of precision (average 3.0%, based on 26 filter pairs), confirming the applicability of the assumption for the sample filters.

2.3.1. Extraction and retention efficiency tests

The extraction efficiency is the ratio of deuterated SVOC or LG mass measured by the GC–MS, to the mass of deuterated compounds spiked onto the sample prior to extraction. Average extraction efficiencies were $74 \pm 32\%$ (PAH-Teflon), $74 \pm 39\%$ (PAH-PUF), $66 \pm 27\%$ (MP-Teflon), $104 \pm 69\%$ (MP-PUF) and $79 \pm 3\%$ (LG-Teflon). PAH and

MP extraction efficiencies are based on the average of all individual species, and the uncertainties are reported as RSDs. SVOC EFs reported here are corrected for sample-specific and compound-specific extraction efficiencies, to account for analytical losses.

Retention efficiencies (a measure of sampling and storage losses) were evaluated by spiking blank Teflon filters and PUF media with deuterated MP or PAH mixtures. These spiked media were then used to collect smoke samples according to procedures described in Section 2.1. They were then extracted and analyzed as described in Section 2.2. The retention efficiency was calculated as the ratio of the mass of deuterated analyte measured in the spiked sampling media, compared to the mass of deuterated analyte originally spiked onto the sampling media.

Average PAH retention efficiencies were $87 \pm 28\%$ (Teflon filters, molecular weight (MW) $\geq 202 \text{ g mol}^{-1}$ only) and $117 \pm 41\%$ (PUFs, excluding d8-naphthalene, for which the retention efficiency was $<20\%$). PAH and MP retention efficiencies are based on the mean of all individual species, and the uncertainties are reported as RSDs. Henceforth, “solid phase PAHs” refer to those with $\text{MW} \geq 202 \text{ g mol}^{-1}$ collected on Teflon filters, and “solid+gas phase PAHs” are the sum of 18 PAHs (naphthalene excluded) collected on Teflon filters and PUFs. The average MP retention efficiencies on PUFs were $81 \pm 39\%$. MP retention efficiencies on Teflon filters were not evaluated in this study, because it has been shown that MPs rapidly evaporate when spiked onto clean Teflon filters (Simpson et al., 2005), and probably migrate to the PUF downstream. The LG retention efficiency was not evaluated, as LG is mainly present in the solid phase (Simoneit, 2002).

2.4. Calculations

Calculation of combustion efficiency (CE: the fraction of carbon released as CO_2) and EFs (pollutant mass emitted per unit mass of dry stubble consumed by fire), including the assumptions that went into these calculations are described in Dhammapala et al. (2006). Background corrected, fire-integrated pollutant concentrations are used for this purpose. Based on propagation of errors, the systematic errors of the SVOC and LG EFs were estimated to be $\pm 30\%$, while EC and OC EFs are within $\pm 25\%$. All uncertainties of results are reported henceforth as 95% confidence intervals.

3. Results and discussion

3.1. Polycyclic aromatic hydrocarbons

The sums of EFs of 19 PAHs in both gas and particle phases were $17 \pm 8.2 \text{ mg kg}^{-1}$ and $21 \pm 15 \text{ mg kg}^{-1}$ for wheat and KBG, respectively. EFs for individual PAHs are included in Table A1 of the electronic supplementary material. The negative correlations between PAH EFs and CE are expected since PAHs are products of incomplete combustion (Fig. 2). Although gas phase PAH EFs from KBG (Fig. 2b) are not well correlated with CE, the wheat data have a R^2 of 0.65.

Some heavier species that are expected to be present mainly in the solid phase at ambient temperatures, were detected in the gas phase (see Table A1). Since average temperatures of the chamber air being sampled ranged from 28 to 53°C (instantaneous chamber temperature reached 97°C), it is likely that phase distributions of some samples had been pushed toward the gas phase at the time of sampling.

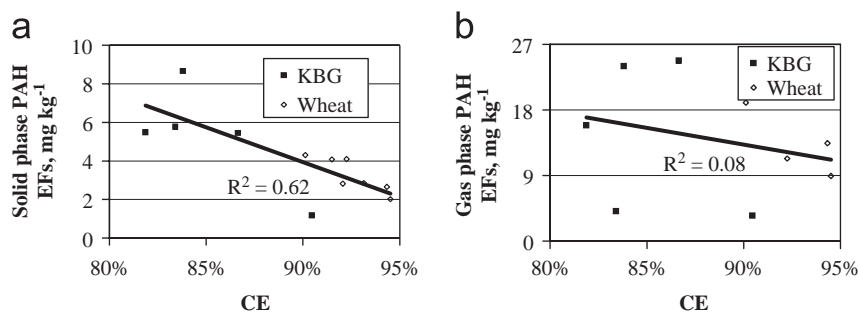


Fig. 2. PAH EFs vs. CE (a) solid phase (b) gas phase. Campaign 4 data only.

Table 2

Summary of PAH, MP, LG, EC and OC EFs for wheat and KBG (PM_{2.5} EFs are provided for comparison purposes)

	Wheat	KBG	Literature ^a
$\sum 19$ PAHs, mg kg ⁻¹	17 ± 8.2 ^b (CE 93 ± 3.3%)	21 ± 15 ^b (CE 85 ± 4.2%)	See Table 3
$\sum 19$ MPs, mg kg ⁻¹	79 ± 36 ^b (CE 93 ± 3.3%)	35 ± 24 ^b (CE 85 ± 4.2%)	
LG, mg kg ⁻¹	150 ± 130 (CE 92 ± 2.7%)	350 ± 510 (CE 86 ± 9.8%)	123 ^c , 65–356 ^d , 303–1,188 ^e , 706–1,940 ^f
EC, g kg ⁻¹	0.35 ± 0.16 (CE 96 ± 2.1%)	0.63 ± 0.056 (CE 90 ± 1.0%)	0.52 ^c , 0.08–0.3 ^d , 0.2–1.3 ^e , 0.8–1.9 ^f , 0.79 ^g , 0.5–1.2 ^h , 0.75 ± 0.5 ⁱ , 0.04–1.5 ^j
OC, g kg ⁻¹	1.9 ± 1.1 (CE 94 ± 3.2%)	6.9 ± 0.85 (CE 90 ± 1.0%)	1.23 ^c , 0.5–1.9 ^d , 8.0–27.8 ^e , 3.0–5.3 ^f , 2.1 ^g , 5.1 ± 2.3 ⁱ , 1.0–15.7 ^j
PM _{2.5} , g kg ⁻¹	3.0 ± 0.60 (CE 95 ± 0.80%)	12.1 ± 1.4 (CE 90 ± 1.0%)	See Dhammapala et al. (2006)

^aWhen several fuels are reported, the EF range is presented for comparison.^bSVOC data from Campaign 4, reported as the sum of solid and gas phases.^cHays et al. (2005), wheat (Campaign 1).^dFine et al. (2004), woodstoves.^eHays et al. (2002), foliar fuels.^fSchauer et al. (2001), fireplace woods.^gTurn et al. (1997), wheat.^hWard and Hardy (1991), logging slash.ⁱFerek et al. (1998), Brazilian grasslands (assuming 50% C in biomass).^jChristian et al. (2003), several woods often burned in Zambia and Indonesia.

Table 3

Comparison with literature: the sum of SVOC EFs in the solid + gas phases, unless otherwise stated. Numbers in parentheses are the # of SVOCs summed

Reference	\sum SVOC EFs ^a , mg kg ⁻¹	This work ^b , mg kg ⁻¹	
		Wheat	KBG
<i>PAHs</i>			
Jenkins et al. (1996a), wheat, CE~85%	20 (17)	16	20
Hays et al. (2005), wheat, dilution sampling during Campaign 1, PM _{2.5} on quartz filter	2 (14)	3.3	5.3
Korenaga et al. (2001), PAH on total PM, rice straw, 10% stubble moisture	2 (7)	1.9	3.9
Ramdahl and Møller (1983), barley	36 (17)	16	20
Hays et al. (2002), foliar fuels	8–26 (5)	8.4	7.6
Schaurer et al. (2001), fireplace woods	34–74 (17)	16	21
<i>MPs</i>			
Hays et al. (2005), as above	5 (13)	6.8	5.4
Hays et al. (2002), as above	372–1167 (10)	48	26
Schauer et al. (2001), as above	1338–1682 (17)	78	35

^aWhen several fuels are reported, the EF range is presented for comparison.^bSum of the same SVOCs in the appropriate phase(s). When solid phase PAHs are compared, only those with MW ≥ 202 g mol⁻¹ are considered.

Tables 2 and 3 summarize and compare the EFs found in this study, against those in literature. Comparison of SVOC EFs against literature is not straightforward since different studies report EFs of different SVOCs. Table 3 lists the sum of individual SVOCs reported in literature, against the sum of the same species in the same phase(s) measured in this work. Wheat and KBG PAH data are in reasonable

agreement with other data for wheat (Jenkins et al., 1996; Hays et al., 2005) when CE differences are accounted for. But wheat and KBG EFs are not always similar to those from burning other types of biomass. Though PAH EFs from rice straw (Korenaga et al., 2001) are comparable, higher PAH EFs have been reported for barley, foliar fuels and fireplace woods.

Higher PAH EFs from barley might be due, in part, to the fact that the barley stubble used by Ramdahl and Møller (1983) had a moisture content of 15% (and therefore a lower CE—see A.S.I., 2003) compared to the wheat and KBG used in this study (9% moisture). Hays et al. (2002—foliar fuels) and Schauer et al. (2001—fireplace woods) both used dilution samplers and quartz filters upstream of PUFs when sampling. We removed the effect of dilution on phase equilibrium and eliminated the quartz filter (adsorption) artifact by summing the EFs of both phases. It is likely that woody fireplace fuels (Schauer et al., 2001) burn at lower CEs. Foliar fuels burned by Hays et al. (2002) had more moisture (8–44%) than wheat and KBG stubble. These factors could partly explain the higher PAH EFs in both foliar fuels and fireplace woods.

3.2. Methoxyphenols

The sums of EFs of 19 MPs in both phases were $35 \pm 24 \text{ mg kg}^{-1}$ and $79 \pm 36 \text{ mg kg}^{-1}$ for KBG and wheat, respectively. EFs for individual MPs (see Table A2 of the electronic supplementary material) show that most of the lighter MPs are in the gas phase.

Although combined solid+gas phase MP EFs appear to show negative correlations with CE (Fig. 3), these relationships are not very strong. Fig. 3 also shows that lower CE KBG burns emit less MPs than the higher CE wheat fires. Because MPs are derived from lignin pyrolysis, the lower lignin content in KBG (1.8%—Sartain, 2004) compared to wheat (11%—Ibrahim, 1998) would

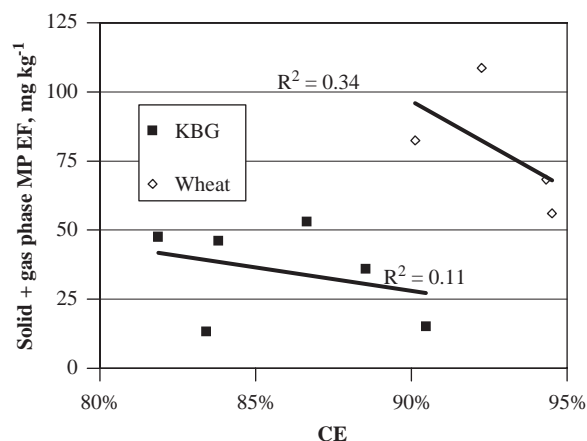


Fig. 3. Solid + gas phase MP EFs vs. CE. Campaign 4 data only.

partly explain the lower MP EFs from KBG, in spite of lower CEs in the latter.

Tables 2 and 3 summarize and compare the MP EFs. Little or no MP EFs have been reported for wheat or KBG stubble burning. MP EFs from foliar fuels (Hays et al., 2002) and fireplace woods (Schauer et al., 2001) are higher than wheat and KBG EFs measured here. In addition to CE differences (see Section 3.1), the high MP EFs from the hard and softwoods used in fireplaces (Schauer et al., 2001) could be partly due to higher lignin content ($20 \pm 4\%$ and $28 \pm 3\%$ lignin in hard and softwoods, respectively, Ibrahim, 1998).

3.3. Levoglucosan

LG EFs are $150 \pm 130 \text{ mg kg}^{-1}$ for wheat and $350 \pm 510 \text{ mg kg}^{-1}$ for KBG. As expected the LG EFs show a strong negative correlation with CE (Fig. 4). LG in wheat and KBG accounts for $2.3 \pm 1.5\%$ and $2.7 \pm 2.0\%$ of the $\text{PM}_{2.5}$, respectively. Though it is difficult to compare KBG EFs due to the wide uncertainties (partly a consequence of having only three samples), the comparison in Table 2 shows that the LG EFs for wheat are similar to wheat data of Hays et al. (2005). CE differences may partly explain the lower wheat EFs compared to other types of biomass.

3.4. EC and OC

3.4.1. KBG

The EC EF was $0.63 \pm 0.056 \text{ g kg}^{-1}$ and the artifact-corrected OC EF was $6.9 \pm 0.85 \text{ g kg}^{-1}$. Both EC and OC show a negative trend with CE (Fig. 5). EC + artifact-corrected OC accounted for $63 \pm 1.9\%$ of the $\text{PM}_{2.5}$ mass. The OC EF vs. CE

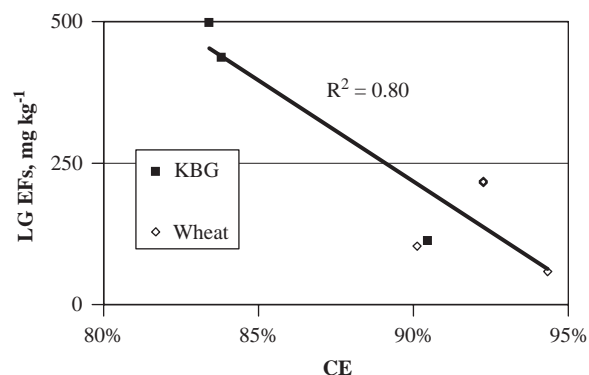


Fig. 4. LG EFs as a function of CE. Campaign 4 data only.

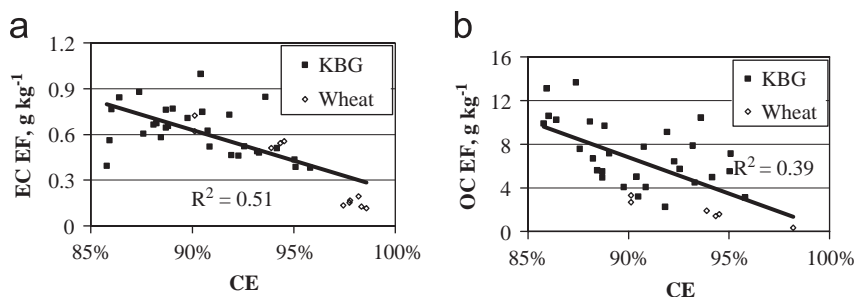


Fig. 5. EFs vs. CE for wheat and KBG (a) EC and (b) OC.

relationship is more scattered than the corresponding EC data, possibly caused by varying amounts of gas phase OC condensing onto solid phase OC (due to differences in chamber temperature). The magnitude of the positive OC artifact, which decreased with increasing Q OC concentration, averaged $5.0 \pm 0.8\%$ of the uncorrected OC.

3.4.2. Wheat

The EC EF was $0.35 \pm 0.16 \text{ g kg}^{-1}$ and the artifact-corrected OC EF was $1.9 \pm 1.1 \text{ g kg}^{-1}$. As with KBG, EC and OC EFs decrease with increasing CE (Fig. 5). These confidence intervals are wider than those reported for KBG, and are a consequence of having fewer samples (see Table 1). EC + artifact-corrected OC accounted for $63 \pm 5.3\%$ of the $\text{PM}_{2.5}$ (as seen in Table 2, $\text{PM}_{2.5}$ EFs for wheat were nearly a factor of 4 lower than KBG). The QbT artifact accounted for $20 \pm 5.5\%$ of uncorrected Q OC.

Table 2 summarizes EC and OC EFs, and compares them against those in literature. EFs from biomass burned in woodstoves are at the lower limit of our data, and this is expected since woodstoves are designed to produce low emissions. Since references cited in Table 2 do not state whether OC data therein have been corrected for adsorption artifacts, it is difficult to comment on the degree of agreement with literature.

4. Conclusions

This work presents some of the first measurements of EFs of SVOCs from KBG stubble burning. On average, the PAH and MP EFs for combined solid + gas phases are $17 \pm 8.2 \text{ mg kg}^{-1}$ and $79 \pm 36 \text{ mg kg}^{-1}$, respectively, for wheat, and $21 \pm$

15 mg kg^{-1} and $35 \pm 24 \text{ mg kg}^{-1}$, respectively, for KBG. LG, particulate EC and artifact-corrected OC EFs are $150 \pm 130 \text{ mg kg}^{-1}$, $0.35 \pm 0.16 \text{ g kg}^{-1}$ and $1.9 \pm 1.1 \text{ g kg}^{-1}$, respectively, for wheat, and $350 \pm 510 \text{ mg kg}^{-1}$, $0.63 \pm 0.056 \text{ g kg}^{-1}$ and $6.9 \pm 0.85 \text{ g kg}^{-1}$, respectively, for KBG. Since EFs of many of these pollutants are inversely correlated with CE, identifying and implementing methods of increasing the CEs of burns would help reduce their emissions from agricultural burning.

Naphthalene (MW 128) cannot be sampled effectively with Teflon filters or PUFs under these conditions, and alternative sampling methods need to be used. The importance of correcting for the adsorption of OC on quartz filters is underscored by the fact that this artifact was seen to positively bias the OC EFs by between 2% and 26%.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.atmosenv.2006.11.023](https://doi.org/10.1016/j.atmosenv.2006.11.023).

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